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Proposed Best Demonstrated Available Technology (BDAT) Background Document for K011, K013, and K014 (Addendum). Volume 14

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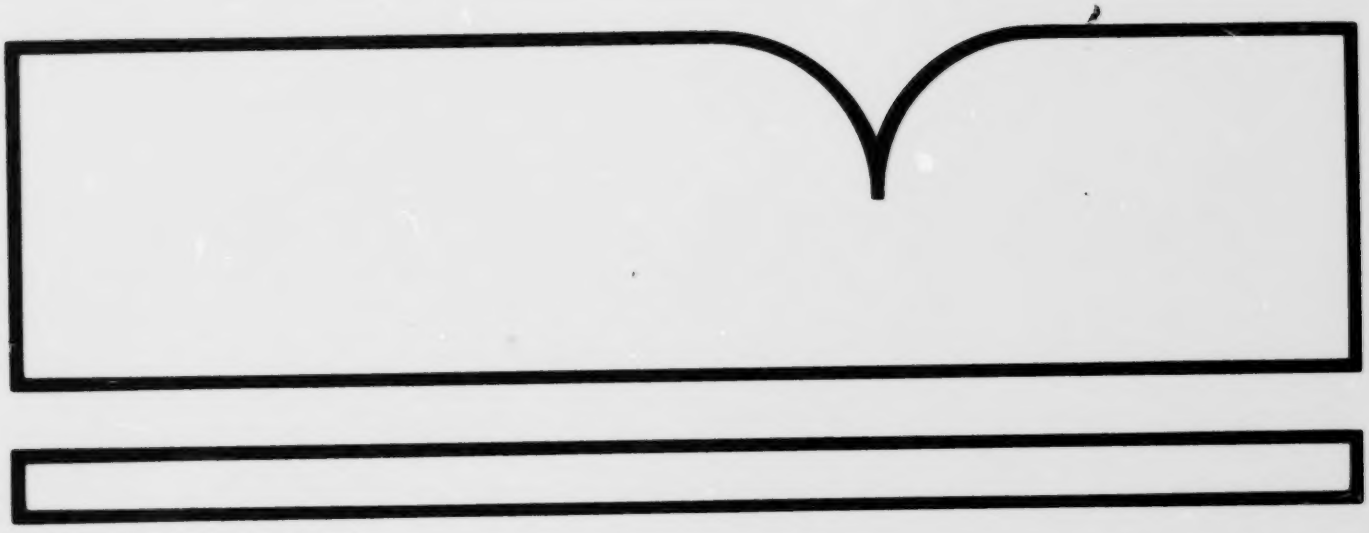

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This document presents the technical support and rationale for the development of treatment standards for K011/K013/K014 wastewaters. Treatment standards for nonwastewater forms of K011/K013/K014 were promulgated in the 2nd 3rds Final Rulemaking on June 23, 1989. This document is an addendum to the June 1989 background document for K011/K013/K014 that accompanied the rulemaking for nonwastewater forms of K011/K013/K014. The Agency is proposing to regulate the same five BDAT list constituents that are regulated in K011/K013/K014 nonwastewaters. These standards are based on the treatment performance of wet air oxidation.

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PROPOSED
BEST DEMONSTRATED AVAILABLE TECHNOLOGY (BDAT) BACKGROUND DOCUMENT FOR K011, K013, AND K014 (ADDENDUM)

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1. EXECUTIVE SUMMARY

This background document presents the technical support and rationale for the development of treatment standards for K011/K013/K014 wastewaters. Treatment standards for nonwastewater forms of K011/K013/K014 were promulgated in the Second Third Final rulemaking (54 FR 26594, June 23, 1989). This background document is issued as an addendum to the June 1989 background document for K011/K013/K014 (USEPA 1989a) that accompanied the rulemaking for nonwastewater forms of K011/K013/K014. Treatment standards for wastewater forms of K011/K013/K014 were not promulgated as part of the First Third rulemaking in order to allow the Agency time for additional data collection and analysis. Information contained in the June 1989 background document is not repeated in this document.

This document presents information specific to the treatment of K011/K013/K014 wastewaters and the technologies that were evaluated in the determination of best demonstrated available technology (BDAT) for K011/K013/K014 wastewaters. The Agency is proposing to regulate the same five BDAT list constituents that are regulated in K011/K013/K014 nonwastewaters (acetonitrile, acrylonitrile, acrylamide, benzene, and cyanide). These standards are based on the treatment performance of wet air oxidation. The proposed treatment standards for K011/K013/K014 wastewaters are presented in Table 1-1.

Compliance with these BDAT treatment standards is a prerequisite for placement of these wastes in units designated as land disposal facilities according to 40 CFR Part 268. For the purpose of determining the treatment standards, K011/K013/K014 wastewaters are defined as wastes containing less than 3.5 percent (weight basis) total organic carbon and less than 1 percent (weight basis) total suspended solids. Information about the wastewater definition is presented in Appendix A.

Table 1-1 BDAT Treatment Standards for K011/K013/K014 Wastewaters

Constituent	Maximum for any single grab sample Total composition (mg/l)
Acetonitrile	38
Acrylonitrile	0.06
Acrylamide	19
Benzene	0.02
Cyanide (total)	21

Wastes not meeting this definition must comply with the treatment standards for K011/K013/K014 nonwastewaters.

Consistent with the background document for nonwastewaters, the treatment performance standard was developed based on a K011/K013/K014 mixed waste. The term K011/K013/K014 can refer to K011, K013, and K014 wastes individually; any combination of K011, K013, and K014 wastes; treatment residuals resulting from treatment of K011, K013, and K014 wastes individually; and treatment residuals resulting from treatment of any combination of K011, K013, and K014 wastes and treatment residuals. Hence, all combinations, and individual wastestreams, if disposed of separately, must meet the treatment standards.

EPA wishes to point out that, because of facility claims of confidentiality, this document does not contain all of the data that EPA used in its regulatory decision-making process. Under 40 CFR Part 2, Subpart B, facilities may claim any or all of the data that are submitted to EPA as confidential. EPA will make determinations regarding the validity of the facility's claim of confidential business information (CBI) according to 40 CFR Part 2, Subpart B. In the meantime, the Agency will treat the data as CBI. Additionally, the Agency would like to emphasize that it evaluated all available data (including CBI data) in developing the BDAT treatment standards for K011/K013/K014 wastewaters.

The BDAT program and EPA's promulgated methodology are more thoroughly described in two additional documents: Methodology for Developing BDAT Treatment Standards (USEPA 1988a) and Generic Quality Assurance Project Plan for Land Disposal Restrictions Program (BDAT) (USEPA 1987a). The petition process to be followed in requesting a variance from the BDAT treatment standards is discussed in the methodology document.

2. INDUSTRIES AFFECTED AND WASTE CHARACTERIZATION

K011, K013, and K014 are waste streams generated by the production of acrylonitrile. K011 is the bottom stream from the wastewater stripper, K013 is the bottom stream from the acetonitrile column, and K014 is the bottom stream from the acetonitrile purification column.

2.1 Industries Affected

The Agency has no new data that would change the description of the acrylonitrile manufacturing industry that was contained in the June 1989 K011/K013/K014 background document (USEPA 1989).

2.2 Waste Characterization

The June 1989 K011/K013/K014 background document contained characterization data for K011/K013/K014 wastes. Additional K011/K013/K014 characterization data submitted after promulgation of the treatment standards for nonwastewaters are presented in Tables 2-1 through 2-5 at the end of this section. The data in the tables were submitted to the Agency by or on behalf of several United States acrylonitrile producers to help EPA characterize the K011/K013/K014 wastewaters.

In the background document for K011/K013/K014 nonwastewaters, it was determined that management of the K011/K013/K014 stream typically involves a settling or filtration process to remove suspended solids followed by deep-well injection of the liquid effluent and land disposal of the filtered solids. The settled filtered solids are considered nonwastewaters, and the liquid effluent is usually considered a wastewater by the generators.

The data in Table 2-1 show that K011 wastewaters typically contain about 400 to 2000 mg/l of acetonitrile, 90 to 1000 mg/l acrylamide, less

than 1020 mg/l acrylonitrile, nondetectable levels of benzene and less than 500 mg/l cyanide. Nickel appears to be present in one K011 wastewater sample; however, the generator of that particular stream claims that the stream is usually filtered to remove suspended catalyst particles containing nickel so these data do not reflect waste characteristics of K011, K013, and K014 wastewaters (Cyanamid 1989c). Wastes defined as K011 also contain 0.85 percent to 3.15 percent total organic carbon (TOC) and 25 to 1100 mg/l total suspended solids (TSS).

The data presented in Table 2-2 show that K013 wastewaters usually contain less than 20 mg/l acetonitrile, less than 100 mg/l acrylamide, less than 20 mg/l acrylonitrile, less than 150 mg/l of cyanide, and nondetectable levels of benzene and nickel. These data show that the TOC range for the K013 wastewaters is 0.29 to 0.55 percent and the TSS range is 2 to 30 mg/l. However, the Agency has confidential data that show the TOC content can average 2 percent (Sterling 1989).

The only additional data for K014 show a waste with about 20,000 mg/l acetonitrile, 3.3 to 8.0 percent TOC, and 8 to 831 mg/l TSS. These data are presented in Table 2-3

The additional data for K011/K013 mixed wastewaters are presented in Table 2-4. Generally, the K011/K013 mixture contains acetonitrile ranging from 180 to 600 mg/l, acrylamide ranging from 500 to 1000 mg/l, acrylonitrile from 10 to 200 mg/l, and less than 1,100 mg/l cyanide. The TOC ranges from approximately 1.4 to 3.0 percent, and TSS ranges from 100 to 550 mg/l.

Table 2-5 presents the available data for the K011/K013/K014 mixture. This waste typically contains 1.1 to 2.0 percent TOC and 20 to 700 mg/l TSS. The K011/K013/K014 mixture usually contains less than 700 mg/l acetonitrile, less than 1600 mg/l acrylonitrile, less than 1100 mg/l acrylamide, less than 0.42 mg/l benzene, and less than 1900 mg/l total cyanide.

In summary, K011, K013, K011/K013, mixtures and the K011/K013/K014 mixtures are aqueous wastes containing low TSS (i.e., less than 1100 mg/l) and low TOC (i.e., less than 3.15 percent). The K014 wastes can contain low TSS (i.e., less than 850 mg/l) and a considerably higher TOC content (i.e., 8.0 percent). Based on these data, the Agency has determined that K011/K013/K014 wastewaters are defined as wastes containing less than 3.5 percent TOC and less than 1 percent TSS; K011/K013/K014 nonwastewaters are defined as all other wastes not meeting this definition. The development of the total organic carbon level is presented in Appendix A of this document.

Table 2-1 Additional K011 Waste Characterization Data

Parameter (units)	Untreated K011 waste (a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(b)
BDAT List Constituents (mg/l)											
Acetone	--	--	--	--	--	--	--	--	--	23.5	--
Acetonitrile	420	1,050	650	533	440	--	--	--	1,700	1,119	--
Acrylamide	780	750	275	87	1,200	--	--	--	1,200	748	--
Acrylonitrile	760	510	330	675	<0.5	2.6	18	47.8±93.5	90	1,020	--
Benzene	--	--	--	--	--	<0.005	<0.005	--	<10	--	--
Cyanide (total)	451	273	506	506	490	--	--	0.3±0.04	302/138	379	
Nickel	--	--	--	--	<.02	<.02	<.02	--	24.3	--	--
Other Analyses											
Ammonia-nitrogen (mg/l)	21,100	12,800	13,900	17,000	17,000	--	--	--	--	--	--
Sulfate (mg/l)	68,400	33,700	42,800	51,000	50,000	--	--	--	--	--	--
Chemical oxygen demand (mg/l)	--	--	--	--	31,000	--	--	--	--	26000	--
Total suspended solids (mg/l)	47	189	25	34	27	--	--	--	--	--	400-1100
Total organic carbon (%)	2.15	1.33	2.03	2.24	1.1	--	--	--	--	1.1	2.6
Total dissolved solids (%)	--	--	--	--	--	--	--	--	--	--	6-15.8

Table 2-1 (continued)

Parameter (units)	Untreated K011 waste																	
	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)
BDAT List Constituents (mg/l)																		
Acetone	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Acetonitrile	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Acrylamide	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Acrylonitrile	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Benzene	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Cyanide (total)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Nickel	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Other Analyses																		
Ammonia-nitrogen (mg/l)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Sulfate (mg/l)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Chemical oxygen demand (mg/l)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Total suspended solids (mg/l)		173	34	25	47	--	--	28	--	--	--	--	--	--	--	--	--	--
Total organic carbon (%)	1.96	2.24	2.03	2.15	1.33	2.01	1.81	2.60	1.51	2.10	1.90	3.15	1.37	1.63	0.85	2.63	1.46	1.93
Total dissolved solids (%)	13.2	9.91	8.05	12.21	8.37	--	6.60	--	--	--	--	--	--	--	--	--	--	--

-- = No reported values.

Sources: a = Tischler/Kocurek 1989.
b = EP 1989a.
c = Cyanamid 1989a.

Table 2-2 Additional K013 Waste Characterization Data (mg/l)

	Untreated K013 waste								
Parameter (units)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(b)
RDAT List Constituents (mg/l)									
Acetonitrile	<1	<1	3	<0.005	--	--	--	19.0	--
Acrylamide	1	10	92	16	--	--	--	--	--
Acrylonitrile	<1	6	2	8.4	2.6	1.2	11.3±7.9	2.2	--
Benzene	--	--	--	--	<0.005	<0.005	--	--	--
Cyanide (total)	12.6	10.6	11.4	11	--	--	108.6±26.5	--	--
Nickel	--	--	--	--	<0.02	<0.02	--	--	--
Other Analyses									
Ammonia-nitrogen (mg/l)	180	150	80	150	--	--	--	235	--
Sulfate (mg/l)	140	80	70	100	--	--	--	--	--
Chemical oxygen demand (mg/l)	--	--	--	13,000	--	--	--	13,440	--
Total suspended solids (mg/l)	5	2	2	9	--	--	--	--	10-30
Total organic carbon (%)	0.55	0.49	0.29	0.52	--	--	--	--	0.4 - 0.5
Total dissolved solids (%)	--	--	--	--	--	--	--	--	0.2 - 0.5

Table 2-2 (continued)

Parameter (units)	Untreated K013 waste										
	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)	(c)
BDAT List Constituents (mg/l)											
Acetonitrile	--	--	--	--	--	--	--	--	--	--	--
Acrylamide	--	--	--	--	--	--	--	--	--	--	--
Acrylonitrile	--	--	--	--	--	--	--	--	--	--	--
Benzene	--	--	--	--	--	--	--	--	--	--	--
Cyanide (total)	--	--	--	--	--	--	--	--	--	--	--
Nickel	--	--	--	--	--	--	--	--	--	--	--
Other Analyses											
Ammonia-nitrogen (mg/l)	--	--	--	--	--	--	--	--	--	--	--
Sulfate (mg/l)	--	--	--	--	--	--	--	--	--	--	--
Chemical oxygen demand (mg/l)	--	--	--	--	--	--	--	--	--	--	--
Total suspended solids (mg/l)	7	2	2	5	18	--	--	--	--	--	--
Total organic carbon (%)	0.42	0.29	0.49	0.55	0.83	0.78	0.81	0.57	1.03	0.65	0.45
Total dissolved solids (%)	0.41	0.25	0.43	0.57	2.34	--	--	--	--	--	--

-- = No reported values.

Sources: a = Tischler/Kocurek 1988.
b = BP 1988a.
c = Cyanamid 1988a.

Table 2-3 Additional K014 Waste Characterization Data (mg/l)

Parameter (units)	Untreated K014 waste (a)	(b)
EDAT List Constituent (mg/l)		
Acetonitrile	11,291.7 ± 9,988.6	--
Other Analyses		
Total organic carbon (%)	--	3.3 - 8.0
Total suspended solids(mg/l)	--	8 - 831

-- = No reported values.

Sources: a = Tischler/Kocurek 1989.
b = EP 1989a.

Table 2-4 Additional K011/K013 Waste Characterization Data (mg/l)

Parameter (units)	Untreated K011/K013 mixed waste (a)	(a)	(a)	(a)	(b)
EDAT List Constituent (mg/l)					
Acetonitrile	575	178	470	329	--
Acrylamide	980	520	797	809	--
Acrylonitrile	50	12	195	162	--
Cyanide (total)	1,100	1,100	1,100	1,100	--
Other Analyses (mg/l)					
Ammonia-nitrogen	6,634	4,390	5,674	5,363	--
Sulfate	17,770	12,017	15,895	16,561	--
Chemical oxygen demand	55.170	35,983	39,652	40,643	--
Total suspended solids	538	322	230	223	100-500
Total organic carbon	--	13,659	15,024	18,244	25,000-30,000
Total dissolved solids	--	--	--		100,000-150,000

-- = No reported values.

Sources: a = Tischler/Kocurek 1989.
b = EP 1989a.

Table 2-5 Additional K011/K013/K014 Waste Characterization Data

Parameter (units)	Untreated K011/K013/K014 mixed waste	
	(a)	(b)
RDAT List Constituents (mg/l)		
Acetonitrile	-	104 - 684
Acrylonitrile	-	550 - 1590
Acrylamide	-	745 - 1078
Benzene	-	0.07 - 0.42
Cyanide (total)	-	1244 - 1899
Other Analyses		
Total suspended solids (mg/l)	20 - 700	-
Total organic carbon (%)	1.1 - 2.0	-
Total dissolved solids (%)	.5 - 7.0	-

- = No reported values.

Sources: a = BP 1989a.
b = BP 1988b.

3. APPLICABLE AND DEMONSTRATED TECHNOLOGIES

For K011/K013/K014 wastewaters, the Agency believes that wet air oxidation is an applicable technology. In addition, the Agency believes biological treatment is applicable for treatment of some K013 wastewaters. The Agency has identified these technologies because they are designed to reduce the concentration of organics and oxidizable inorganics such as cyanide in wastewaters. EPA also believes that carbon adsorption is applicable as a polishing step for both wet air oxidation and biological treatment to reduce the organic compounds in the effluents.

Wet air oxidation is potentially applicable for wastewaters containing up to 10 percent organic concentration (USEPA 1987b). It is a treatment technology that oxidizes hazardous organic compounds at elevated temperatures and pressures. The Agency notes that the term "wet air oxidation" is used throughout this document to identify a process whereby wastes are oxidized in an aqueous liquid phase under conditions of elevated temperature and pressure. The oxidant could be air, oxygen- enriched air, "pure" oxygen, or other oxidants.

Biological treatment is a technology that uses living microorganisms to decompose organic constituents into carbon dioxide, water, and simple organic compounds. It is generally applicable for wastewaters containing dilute concentrations of organics.

Carbon adsorption is a technology in which the wastewater is passed through a column packed with activated carbon. The contaminants in the wastewaters are adsorbed by the carbon because the contaminant has a low solubility in the waste and/or the contaminant has a greater affinity for the carbon than for the waste.

The Agency believes that wet air oxidation is demonstrated to treat the BDAT list organics and cyanide present in the K011/K013/K014 nonwastewaters. The Agency has identified several facilities performing pilot-scale wet air oxidation tests on K011/K013/K014 wastewaters. Furthermore, wet air oxidation is a proven full-scale technology for destroying organics and cyanides in numerous hazardous waste streams (USEPA 1987b). Hence, the Agency believes that wet air oxidation is demonstrated for K011/K013/K014 wastewaters.

It is believed that biological treatment is not applicable for K011, K011/K013 mixtures, or K011/K013/K014 mixtures because of the much greater concentrations of organic constituents (i.e., up to 3.1 percent) and ammonium sulfate. Additionally, the organic concentration of K014 is too high (i.e., up to 8.0 percent) for biological treatment to be effective (USEPA 1987b). Moreover, some K013 wastes contain approximately 2 percent TOC and biological treatment would not be applicable because of the organic content.

EPA believes that biological treatment is demonstrated to treat some K013 wastewaters. The Agency has identified one facility testing biological treatment for K013 wastewaters containing low concentrations of BDAT list organics; thus the Agency considers biological treatment to be demonstrated to treat K013 wastewaters containing low concentrations of organics. However, the Agency believes that it is inappropriate to identify biological treatment as demonstrated for K011/K013/K014 wastewaters based solely on the biological treatment of dilute K013 wastewaters because K011/K013/K014 wastewater streams consisting of K011 and K013 combined or K011, K013, and K014 combined would contain much higher concentrations of dissolved ammonia and sulfate. It is conceivable that the high concentrations of dissolved ammonia and sulfate would interfere with biological treatment. Additionally, because some K013 wastewaters are known to contain TOC concentrations of 2 percent (Sterling 1989), biological treatment would be inappropriate.

The Agency has not identified any facilities performing carbon adsorption treatment on K011/K013/K014 wastewaters. Consequently, EPA does not believe that carbon adsorption is demonstrated to treat these wastes. Detailed discussions of wet air oxidation, biological treatment, and carbon adsorption are presented in the Treatment Technology Background Document (USEPA 1988b).

4. PERFORMANCE DATA

This section presents the data available to EPA on the performance of demonstrated technologies in treating K011/K013/K014 wastewaters. These data are used elsewhere in this document for determining which technologies represent BDAT (Section 5), for selecting constituents to be regulated (Section 6), and for developing treatment standards (Section 7). Eligible data, in addition to full-scale demonstration data, may include data developed at research facilities or obtained through other applications at less than full- scale operation, as long as the technology is demonstrated in full-scale operation for similar wastes.

Performance data, to the extent that they are available to EPA, include the untreated and treated waste concentrations for a given constituent, values of operating parameters that were measured at the time the waste was being treated, values of relevant design parameters for the treatment technology, and data on waste characteristics that affect performance of the treatment technology.

Tables 4-1 through 4-6 present performance data for wet air oxidation treatment of K011/K013/K014 wastewaters. All six evaluations were performed using different process equipment, operating conditions, and waste matrices.

Table 4-1 contains treatment performance data for pilot-scale treatment of K011/K013/K014 mixed waste by a proprietary wet air oxidation process. The data consist of four sets of untreated and treated wastewater effluent samples. These data show reductions of the organics and cyanide concentrations in the wastewater effluent. The operating conditions and all process information have been classified as Confidential Business Information (CBI) and cannot be presented in the K011/K013/K014 addendum. These data are located in the RCRA CBI docket.

Table 4-2 presents performance data for treatment of K011 wastewaters by wet air oxidation process. These data consist of one set of untreated K011 wastewater and treated wastewater effluent sample results. Concentration of organics have been reduced from concentrations as high as 1700 mg/l to 77 mg/l and total cyanide has been reduced from 302 mg/l to 7.1 mg/l. Operating data collected during the test are also shown on the table.

The data in Table 4-3 show the performance of wet air oxidation for treatment of K011/K013 mixed wastes. These data consist of one untreated sample result and eight different treated effluent sample results. The same untreated waste was treated using eight different combinations of operating conditions. The operating conditions are shown in the table for each separate test. The results show reductions for acetonitrile and total cyanide during all tests. Test #4 reported an increase in acrylonitrile concentration, while test #2, test #3, test #5, and test #8 reported an increase in acrylamide concentration.

Table 4-4 presents performance data for treatment of another K011/K013 mixed waste. For this evaluation there are three sets of untreated and treated results. Test #1 shows reductions for all constituents except acrylamide. Test #2 and Test #3 show reductions for all constituents. The operating conditions are shown in the table.

Table 4-5 presents performance data for the laboratory-scale wet air oxidation process of K011 waste. The data consist of one untreated sample and the results of two treated wastewater effluents generated at different operating temperatures. The results show reductions of certain organic constituents and cyanide; however, both treated effluents show increases in the total organic carbon content.

Table 4-6 presents wet air oxidation performance data for treatment of K011, K013, and mixtures of the two streams. The operating conditions are shown on the table and are constant for all three evaluations. The

first evaluation consists of two sets of untreated and treated results for K011/K013 mixed wastes. Reductions are noted for all four organic constituents and cyanide. The second evaluation is for treatment of K013 waste. These data consist of one set of untreated and treated results. The concentration of acetonitrile increased in the treatment effluent, while the other three organics and cyanide concentrations decreased. For the K011 wastewater, reductions in the constituents of concern in the treatment effluent are shown for all four organics consistuents and cyanide.

Table 4-1 Performance Data for K011/K013/K014 Treatment
by a Proprietary Wet Air Oxidation Process

	Test number							
	Test #1		Test #2		Test #3		Test #4	
Parameter (units)	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
BDAT List Constituent (mg/l)								
Acetonitrile	166	3.8	229	3.3	104	13.8	684	11.8
Acrylonitrile	1,560	<0.02	1,590	<0.02	728	<0.02	550	<0.02
Benzene	0.17	0.007	0.18	0.007	0.07	<.006	0.42	<.006
Acrylamide	844	2.59	770	1.81	1,078	5.54	745	8.24
Cyanide (total)	1,244	3.9	1,300	4.0	1,460	0.7	1,899	4.6
Other Analyses (mg/l)								
pH	5.9	2.0	6.0	2.0	5.9	7.1	5.9	7.2
Chemical oxygen demand	55,900	3,300	57,200	4,100	60,900	3,800	47,900	3,400
Total organic carbon	20,700	1,700	20,600	2,100	22,300	2,100	14,800	1,800
Operating Conditions:								
Reactor temperature: CBI								
Residence time: CBI								
Off-gas oxygen concentration: CBI								
Reactor pressure: CBI								

CBI = Confidential Business Information.

Reference: BP 1989b.

Table 4-2 Performance of Wet Air Oxidation on K011 Wastes

Parameter (units)	Untreated	Treated
BDAT List Constituent (mg/l)		
Acetonitrile	1,700	77
Acrylonitrile	90	<10
Acrylamide	1,200	<20
Benzene	<10	<10
Cyanide (total)	302	7.1
Cyanide (amenable)	138	<1

Operating conditions: Reactor temperature: 280°C
Residence time: 60 minutes
Off-gas oxygen concentration: unknown
Reactor pressure: 3,300 psig

Reference: Tischler/Kocurek 1989.

Table 4-3 Performance of Pilot-Scale Wet Air Oxidation on K011/K013 Wastes

Parameters (units)	Untreated K011/K013	Treated K011/K013 Test #1	Test #2	Test #3	Test #4	Test #5	Test #6	Test #7	Test #8
BDAT list constituents (mg/l)									
Acetonitrile	575	110	254	245	270	295	0	407	215
Acrylamide	980	0	1120	1205	107	1007	200	69	1057
Acrylonitrile	50	1	0	12	100	0	20	43	8
Cyanide (Total)	1100	2.4	2.2	0.3	5	2.5	0.8	1.7	0
Other analyses (mg/l)									
Ammonia-nitrogen	8634	10923	10760	10741	10829	10894	10984	10683	9424
Sulfate	17770	19094	18037	18494	18285	17571	19220	17183	15676
Chemical oxygen demand	55170	20220	19463	18293	23013	22047	19315	22839	33475
Total suspended solids	538	1461	1263	915	1527	1210	897	1468	1961
Total organic carbon	20488	12390	12390	10927	13366	12195	10927	12488	14829
Operating conditions									
Reactor temperature (°C)		249	260	260	238	238	249	249	249
Residence time (minutes)		70	70	70	70	70	70	52	60
Off-gas oxygen (percent)		3	3	6	3	6	6	3	0
Reactor pressure (psig)		900	1100	1100	900	900	900	900	900

Source: Tischler/Kocurek 1989.

Table 4-4 Performance of Pilot-Scale Wet Air Oxidation on K011/K013 Wastes

Parameter (units)	Test Number					
	Test #1		Test #2		Test #3	
	Untreated	Treated	Untreated	Treated	Untreated	Treated
BDAT List Constituents (mg/l)						
Acetonitrile	178	221	470	50	329	114
Acrylamide	520	972	787	156	809	12
Acrylonitrile	12	11	195	5	162	13
Total cyanide	1100	0.6	1100	2.1	1100	1.7
Others Analyses (mg/l)						
Ammonia-nitrogen	4390	7698	5644	7883	5363	9151
Sulfate	12017	11816	15895	17434	16561	17628
Chemical oxygen demand	35983	16539	39652	19639	40643	18961
Total suspended solids	322	790	230	839	223	932
Total organic carbon	13659	12098	15024	7317	18244	9951
Operating Conditions						
Reactor temperature (°C)		249		249		249
Residence time (minutes)		70		70		60
Off-gas oxygen (percent)		3		3		3
Reactor pressure (psig)		900		900		900

Reference: Tischler/Kocurek 1989.

Table 4-5 Performance of Laboratory-Scale Wet Air Oxidation on K011 Wastes

Parameter (units)	Untreated	Treated Test #1	Treated Test #2
BDAT List Constituents (mg/l)			
Acetonitrile	1119	255	399
Acrylamide	748	143	186
Acrylonitrile	1020	21	32
Total cyanide	379	0.63	3.1
Others Analyses (mg/l)			
Chemical oxygen demand	26000	5760	6540
Total organic carbon	11000	13090	15160
Operating Conditions			
Reactor temperature (°C)		290	270
Residence time (minutes)		120	120
Reactor pressure (psig)		2540	2540

Reference: Tischler/Kocurek 1989.

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Table 4-6 Wet Air Oxidation of K011, K013, and Mixtures of the Two Streams

Parameter (units)	K011/K013 mixed wastes				K013		K011	
	Test #1		Test #2		Test		Test	
	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
RDAT List Constituents (ppm)								
Acetonitrile	690	15.5	720	11.4	0.40	50	1160	10
Acrylonitrile	420	0.85	215	0.2	1.30	0.30	380	0.04
Acrylamide	680	<1	690	<1	6	<1	1260	<1
Benzene	<5	0.006	<5	0.01	<0.01	<0.01	<5	<0.01
Cyanide (total)	90	0.75	120	0.56	25.7	0.05	373	0.09
Operating Conditions								
Reactor temperature (I)	280							
Residence time (minutes)	60							
Off-gas oxygen	--							
Reactor pressure (psi)	1000							

Reference: Cyanamid 1988b.

5. IDENTIFICATION OF BEST DEMONSTRATED AVAILABLE TECHNOLOGY (BDAT)

This section presents the Agency's rationale for determining the best demonstrated available technology (BDAT) for K011/K013/K014 wastewaters. The Agency examines all available performance data on technologies that are identified as demonstrated for treatment of K011/K013/K014 wastewaters.

The performance data are evaluated according to the BDAT Methodology (USEPA 1988). First, the available design and operating data are examined to ensure proper design and operation of the treatment system. Data that indicate that the treatment system was not well-designed and well-operated at the time of testing are not used in the determination of BDAT. Next, the "best" performing treatment technology is evaluated to determine whether the resulting treatment is substantial. If the "best" technology provides substantial treatment and it has been determined that the technology is also available to the affected industry, then the technology represents BDAT.

The only demonstrated technology identified for treatment of K011/K013/K014 wastewaters is wet air oxidation, hence, it is "best." The Agency has treatment performance data from several different wet air oxidation processes. Upon examination of the performance data, it was determined that some data showed that organic constituent concentrations increased in value after treatment. Consequently, EPA determined that the operating conditions for those tests were not optimized and deleted these data from the evaluation of substantial treatment. The deleted data sets include data from Table 4.3, Test #2, Test #3, Test #4, Test #5, and Test #8; data in Table 4.4, Test #1; and all data in Table 4.5.

Using the remaining wet air oxidation performance data, EPA's determination of substantial treatment for organics is based on the reduction of BDAT list organic constituents from levels as high as 1590 mg/l to levels of less than 0.02 mg/l in the wastewater effluent. EPA's determination of substantial treatment for cyanide is based on the reduction of total cyanide from levels as high as 1899 mg/l to levels of less than 4.6 mg/l in the wastewater effluent.

The Agency believes that these reductions are substantial and that wet air oxidation is available to treat organics and cyanide present in the K011/K013/K014 wastewaters because the technology is commercially available. The Agency notes that one of the wet air oxidation processes is proprietary; however, the company has stated in writing that it "... is fully committed to the commercial availability of this technology" (BP 1989c). Therefore, EPA believes that wet air oxidation represents BDAT for the organics and cyanide present in the K011/K013/K014 wastewaters.

6. SELECTION OF REGULATED CONSTITUENTS

The Agency presented its selection of regulated constituents for K011/K013/K014 nonwastewaters in Section 6 of the K011/K013/K014 background document (USEPA 1989). These regulated constituents are acetonitrile, acrylonitrile, acrylamide, benzene, and cyanide.

The Agency has no data that would lead it to believe that K011/K013/K014 wastewaters would contain other constituents that may warrant regulation. Furthermore, it is clear from examination of the performance data presented earlier in this addendum that wet air oxidation substantially treats each of the above regulated constituents in K011/K013/K014 wastewaters. Therefore, the Agency is selecting the same regulated constituents for the purpose of regulating K011/K013/K014 wastewaters that were selected for K011/K013/K014 nonwastewaters.

7. DEVELOPMENT OF BDAT TREATMENT STANDARDS

This section presents the calculation of treatment standards for the regulated constituents described in Section 6. These standards are calculated based on the performance of the demonstrated treatment system that was determined to be BDAT (i.e., wet air oxidation). Analytical methods used to calculate concentrations of the regulated constituents are discussed in Appendix B.

Consistent with the background document for K011/K013/K014 nonwastewaters, the Agency used only treatment performance data for mixed K011/K013/K014 wastes to develop the numerical performance standards. Therefore, data in Table 4-2, and some data in Table 4-6 will not be used in the standard calculations. The rationale for developing the standards as a mixture is described in the K011/K013/K014 background document (USEPA 1989).

As discussed in the methodology (USEPA 1989), the Agency calculates the treatment performance standards by following a four-step procedure: (1) correcting the remaining performance data for analytical interference; (2) editing the data; (3) calculating adjustment factor (variability factors) to account for process variability; and (4) calculating the actual treatment standards using variability factors and average treatment values. The four steps in this procedure are described in detail in Sections 7-1 through 7-4

7.1 Correcting the Remaining Data

After the data were deleted in Section 5 because of the poor operating conditions and single waste stream performance data were deleted, the data remaining to be used in the calculation consisted of treatment data in Table 4-1, some data in Table 4-3, some data in Table 4-4, and some data in Table 4-6. All data values were corrected in

order to take into account analytical interferences associated with the chemical make-up of the treated samples. This was accomplished by calculating an accuracy factor from the percent recoveries for the selected regulated constituents in the K011/K013/K014 wastewaters. The actual recovery values, accuracy factors, and corrected concentrations for the selected constituents are presented in Appendix B. The corrected concentration values were obtained by multiplying the accuracy factors by the concentration values in the treated waste.

7.2 Editing Data

In order to use all the remaining performance data to calculate treatment standards, the Agency must determine whether the data are homogeneous (i.e., represent approximately the same treatment efficiencies). The remaining performance data for wet air oxidation treatment of K011/K013/K014 wastewaters are contained in Section 4 of this addendum. It should be noted that each table contains data for a different wet air oxidation technology operated at different levels of temperature, pressure, and reactor residence time. In particular, the wet air oxidation technology used to produce the data in Table 4.1, which is claimed to be proprietary by BP Chemicals Inc., differs in certain aspects from the wet air oxidation technologies used to produce the data in Tables 4-3, 4-4, and 4-6.

The data in Table 4-1, Table 4-3, Table 4-4, and Table 4-6 were compared by using an analysis of variance (ANOVA) test to reveal whether the treatment performance represented by each system is homogeneous to the treatment performance represented by the other systems. The ANOVA calculation is presented in Appendix C. The ANOVA test proved that the system represented by the data in Table 4-1 is not homogeneous with the other data and demonstrates significantly better treatment. Therefore, the Agency is using only Table 4-1 data to develop the treatment standards for K011/K013/K014 wastewaters.

7.3 Calculating Variability Factors

It is expected that in normal operation of a well-designed and well-operated treatment system, there will be some variability in performance. Based on the test data, a measure of this variability is expressed by the variability factor. The methodology for calculating variability factors is explained in the BDAT Methodology document (USEPA 1989). Table 7-1 presents the results of the variability calculations for the selected constituents in K011/K013/K014 wastewaters.

In instances where a selected constituent was not detected in the treated waste, the treated value for that constituent was assumed to be at the detection limits. For example, acrylonitrile was not detected in the treated wastewater effluent and concentration values were set at the detection limit. This resulted in no apparent variation among the treated values and a calculated variability factor of 1.0. A variability factor of 1.0 represents test data from a process measured without variation and analytical interferences. Instead of using the calculated value of 1.0, the variability factors for acrylonitrile were fixed at 2.8 as justified in the methodology document (USEPA 1988a).

7.4 Calculating the Treatment Standards

The treatment standards for the selected constituents were determined first by calculating an arithmetic average value for the accuracy-corrected concentrations of each constituent. Next, the variability factors were multiplied by the average concentration values. The treatment standards are presented in Table 7-1.

Table 7-1. Calculation of Treatment Standards for Acrylonitrile Wastewaters

Wastewater constituents	Effluent concentrations (mg/l) #1	#2	#3	#4	Percent recovery	Accuracy* correction factor	Corrected average	Variability factor	Treatment Standard ** (mg/l)
Acetonitrile	3.8	3.3	13.8	11.8	100	1	8.2	4.66	38
Acrylonitrile	<0.02	<0.02	<0.02	<0.02	100	1	0.02	2.8	0.06
Acrylamide	2.59	1.81	5.54	8.24	100	1	4.55	4.22	19
Benzene	0.007	0.007	<0.006	<0.006	53	1.89	0.012	1.24	0.02
Cyanide (total)	3.9	4.0	0.70	4.6	100	1	3.3	6.47	21

* Accuracy Correction Factor = 100/percent recovery.

**Treatment standard = (Accuracy-corrected average concentration) X (variability factor)

8. REFERENCES

BP. 1988. BP Chemical America Inc. Letter dated August 31, 1988, from S. Schoger (BP) to J. Berlow (EPA) and attached report. (The attached report is CBI.)

BP. 1989a. BP Chemicals Inc. Letter dated August 15, 1989, from P. Huff (BP) to L. Rosengrant (EPA).

BP. 1989b. BP Chemicals Inc. Letter dated July 28, 1989, from K. Madliger (BP) to L. Rosengrant (EPA) and attached report, Demonstration of a wet oxidation process for treating acrylonitrile wastewater, by BP Chemicals Inc., dated June 1989.

Cyanamid. 1989a. Letter dated September 11, 1989, from J. Schneller (Cyanamid) to M. Chatmon-McEaddy (EPA).

Cyanamid. 1989b. Letter dated September 7, 1989, from J. Schneller (Cyanamid) to M. Chatmon-McEaddy (EPA).

Cyanamid. 1989c. American Cyanamid. Letter dated August 2, 1989, from J. Schneller (Cyanamid) to M. Chatmon-McEaddy (EPA).

Gilbert, Richard D. 1987. Statistical methods for environmental pollution monitoring. NY: Van Nostrand. pp. 174-5.

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USEPA. 1987a. U.S. Environmental Protection Agency. Generic quality project plan for Land Disposal Restrictions Program ("BDAT"). Washington, D.C.: U.S. Environmental Protection Agency.

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USEPA. 1988b. U.S. Environmental Protection Agency. Treatment technology background. Washington, D.C.: U.S. Environmental Protection Agency.

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APPENDIX A

DETERMINATION OF WASTEWATER DEFINITION FOR K011/K013/K014 WASTES

For the purpose of determining the applicability of the BDAT treatment standards, the Agency defines wastewaters as wastes containing less than 1 percent (weight basis) total suspended solids (TSS) and less than 1 percent (weight basis) total organic carbon (TOC). Wastes not meeting this definition must comply with treatment standards for nonwastewaters. Additionally, the treatment performance data used to develop standards for nonwastewaters and wastewaters are typically based on untreated wastes as defined above. Below is a brief discussion about the rationale used by EPA to extend the wastewater definition for K011/K013/K014 wastes, so that it includes wastes that contain up to 3.5 percent TOC.

The Agency identified incineration as BDAT for K011/K013/K014 nonwastewaters in the Second Third rulemaking (54 FR 26594, June 23, 1989), basing its identification on performance data for incineration of K011/K013/K014 sludge that had resulted from allowing as-generated K011/K013/K014 wastes to settle in a settling basin. The K011/K013/K014 sludge was the bottoms (underflow) stream from the settling basin. This waste consisted of 17 to 31 percent TOC and approximately 10 to 40 percent TSS.

Since making the determination of BDAT for K011/K013/K014 nonwastewaters, the Agency has collected additional data regarding K011/K013/K014 waste characterization and treatment; these additional data are reported in Sections 2 and 4 of this addendum. The waste characterization section of this addendum shows that many as-generated K011/K013/K014 wastes consist of between 1 percent and 3 percent by weight total organic carbon and less than 1 percent by weight total suspended solids.

The Agency does not believe that incineration is BDAT for most as-generated K011/K013/K014 wastes because of the large volume and low Btu content of those wastes. It would require extensive amounts of energy and incineration capacity to incinerate these aqueous wastes. However, the K011/K013/K014 as-generated wastes are ideal candidates for wet air oxidation because of the relatively low organic content (compared to most incinerated wastes), low TSS, and aqueous nature. Additionally, EPA has treatment performance data for only wet air oxidation for the K011/K013/K014 wastes as-generated. EPA does not have performance data for incineration of the wastes as-generated, and has no treatment data for wastes defined as wastewaters by the original BDAT definition.

The Agency is proposing to extend the definition of wastewaters for K011/K013/K014 wastes to include wastes containing less than 3.5 percent TOC and less than 1 percent TSS so that the wet air oxidation data can be used to develop standards (rather than designate incineration as the BDAT). The Agency determined the upper limit of 3.5 percent based on a calculation of the 99th percentile for all the available TOC values for mixed K011/K013/K014 waste streams. Mixed waste streams have been used as the basis in the development of the nonwastewater and wastewater standards for reasons presented in the background document for K011/K013/K014 (USEPA 1989). The calculation for the 99th percentile is presented in Table A-1. The data used in the calculation are presented in Section 2. When the data was reported as a range of values, the Agency used the lowest and highest value in the calculation. The actual value is 3.3 percent, but the Agency rounded to 3.5 for analytical convenience.

Actual forms of various K011/K013/K014 wastes as-generated depend on process configurations and operating parameters, both of which differ somewhat among acrylonitrile producers. Although the Agency defines BDAT as wet air oxidation for wastes containing less than 3.5 percent TOC and less than 1 percent TSS for K011/K013/K014, this does not prevent wet air oxidation treatment of a waste containing 8 percent TOC as long as the residual wastewater (i.e., wastewaters with less than 3.5 percent TOC and less than 1 percent TSS) can achieve the levels set for K011/K013/K014 wastewaters. Also any nonwastewater residuals must meet the standards established for nonwastewaters. It is the chemical characteristics of the waste to be land-disposed (not the waste prior to treatment) that dictate which numerical standards must be met.

Table A-1 Calculation of 99th Percentile of Total Organic Carbon (TOC) Content

Source	Total organic carbon (TOC) (mg/l)	Waste matrix
Tischler/Kocurek	20,488	K011/K013
Tischler/Kocurek	13,659	K011/K013
Tischler/Kocurek	15,024	K011/K013
Tischler/Kocurek	18,244	K011/K013
BP July 18, 1989	20,700	K011/K013/K014
BP July 18, 1989	20,600	K011/K013/K014
BP July 18, 1989	22,300	K011/K013/K014
BP July 18, 1989	14,800	K011/K013/K014
BP July 18, 1989	30,000	K011/K013
BP July 18, 1989	20,000	K011/K013/K014

The original data are approximately normally distributed with a possible outlier (i.e., the 30,000 mg/l value). The log-transformed data are more normally distributed with no suspected outlier. Using log-transformed data, a 99th percentile estimate of TOC equaling 3.3 percent is obtained from the following equation:

$$\text{99th percentile TOC} = \exp(\bar{y} + Z_{99}Sy) = \exp(9.858 + 2.326 \times 0.232) \approx 33,000$$

where:

$y = \ln X$

X = TOC (mg/l)

$\bar{y}$ = average log TOC

Sy = standard deviation log TOC

Z_{99} = 99th percentile value of the standard normal variate.

Reference: Richard J. Gilbert. 1987.

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APPENDIX B

Analytical Information

The analytical methods used for analysis of the regulated constituents identified in Section 6 are listed in Table B-1. SW-846 methods (EPA's Test Methods for Evaluation of Solid Waste; Physical/Chemical Methods, SW-846, Third Edition, November 1986) were used in determining total constituent concentrations except for the acrylamide analysis.

Acrylamide was determined by a Waters 600 HPLC with a Waters 494 UV detector at 218 nm. Samples were analyzed by direct injection onto a Chromegabond C_{22} (30 cm x 4.6 mm) column and eluted with methanol-acetonitrile-water eluent. Analyte identification and quantification were based on retention time matching to external standards. Multipoint external standard calibration to the UV detector was used to quantify the amount of acrylamide present. Calibration included determination of instrumental response over a range of standard concentrations. Instrumental calibration was routinely checked by the analysis of a mid-range standard. The acceptance criteria were established at 15 percent relative percent difference for the absolute instrumental response of a calibration check standard relative to initial calibration data. If results were outside the 15 percent range, calibration was reestablished.

As stated in the BDAT methodology, concentrations for the regulated constituents will be corrected to account for analytical interference associated with the chemical makeup of the waste matrix. The correction factor for a constituent is based on the matrix spike recovery values. Table B-2 presents the available matrix spike recoveries used to determine the correction factors for some wastewater organic and cyanide data. It should be mentioned that if a recovery value is above

100 percent, the Agency uses 100 percent to determine the accuracy adjustment so that the adjusted values do not decrease when corrected for accuracy. EPA believes this is a conservative approach for calculating treatment standards. For the Cyanamide data, values were not available for all volatile organic constituents (i.e., acetonitrile). Therefore, the Agency used an average percent recovery to calculate the accuracy correction factor for acetonitrile.

Table B-1 Analytical Methods for Regulated Constituents in K011/K013/K014 Wastes

Regulated constituents	Extraction method	Method number	Analytical method	SW-846 Method number
Volatile				
Acetonitrile	Purge and trap	5030	Gas Chromatography/Mass Spectrometry	8030
Acrylonitrile	Purge and trap	5030	Gas Chromatography/Mass Spectrometry	8030
Acrylamide	Direct injection		HPLC*	
Benzene	Purge and trap	5030	Gas Chromatography/Mass Spectrometry	8030
Inorganics Other Than Metals				
Cyanide (total)	Specified in analytical method		Colorimetric	9012

*A high-performance liquid chromatography (HPLC) method has been used to perform acrylamide analysis. More information about the method is described in the text of this Appendix.

References: BP 1989b.

Table B-2 Matrix Spike Recoveries Used to Calculate Corrections Factors for Wet Air Oxidation Treated Wastewaters

Data source	Constituent	Original sample	Spike added	Sample: Spike result	Sample: Percent recovery*	Accuracy correction factor**
Cyanamide 1989b	Acrylonitrile	0.65 ppm	0.20 ppm	1.04 ppm	195	1.00
	Acrylonitrile	0.20 ppm	0.20 ppm	0.46 ppm	130	1.00
	Benzene	0.006 ppm	0.22 ppm	0.256 ppm	113	1.00
	Benzene	0.01 ppm	0.218 ppm	0.201 ppm	88	1.14
	Acrylamide	<1 ppm	50 ppm	56 ppm	113	1.00
	Acetonitrile	--	--	--	128 (average)	1.00
	Cyanide (total)	0.75 ppm	5.0 ppm	5.05 ppm	86	1.16
BP 1989b	Acetonitrile	3.8 ug/l	1.7 ug/l	7.2 ug/l	197	1.00
	Acrylonitrile	14 ug/l	420 ug/l	597 ug/l	139	1.00
	Acrylamide	554 mg/l	1990 mg/l	2640 mg/l	105	1.00
	Benzene	8.1 ug/l	52 ug/l	36 ug/l	53	1.89
	Cyanide (total)***	0.6 mg/l	0.1 mg/l	0.7 mg/l	100	1.00

* Percent recovery = [(Spike Result - Original Amount)/Spike amount] x 100.

** Accuracy correction factor = 100/Percent Recovery (using the lowest percent recovery values).

*** The recovery results for cyanide are actually for the product feed and not the treated waste. They are used since they are the only spike recoveries presented for cyanide.

APPENDIX C

ANOVA Test

EPA is using the statistical method known as an analysis of variance (ANOVA) in the determination of the level of performance that represents the best treatment. Since the Agency has data from more than one wet air oxidation process, this method provides a measure of the differences between data sets. If the differences are not statistically significant, the data sets are said to be homogeneous.

If the Agency found that the levels of performance for one or more wet air oxidation processes are not statistically different (i.e., the data sets are homogeneous), EPA would average the long term performance values achieved by each wet air oxidation process and then multiply this value by the largest variability factor associated with any of the acceptable wet air oxidation processes. If EPA found that one process performs significantly better (i.e., the data sets are not homogeneous), BDAT would be the level of performance achieved by the best wet air oxidation process multiplied by its variability factor.

To determine whether any or all of the treatment performance data sets are homogeneous using the analysis of variance method, it is necessary to compare a calculated "F value" to what is known as a "critical value" (see Table C-1). These critical values are available in most statistics tests (see, for example, Statistical Concepts and Methods by Bhattacharyya and Johnson, 1977, John Wiley Publications, New York).

Where the F value is less than the critical value, all treatment data sets are homogeneous. If the F value exceeds the critical value, it is necessary to perform a "pair wise F" test to determine whether any of the

sets are homogeneous. The "pair wise F" test must be done for all of the various combinations of data sets using the same method and equation as the general F test.

The F value is calculated as follows:

(i) All data are natural logtransformed.

(ii) The sum of the log transformed data points for each data set is computed (T_i).

(iii) The statistical paramater known as the sum of the squares between data sets (SSB) is computed:

$$SSB = \left[\sum_{i=1}^{k} \left(\frac{T_i^2}{n_i} \right) \right] - \left[\left(\frac{\sum_{i=1}^{k} T_i}{N} \right)^2 \right]$$

k = number of different wet air oxidation processes
n_i = number of data points for wet air oxidation process i
N = number of data points for all wet air oxidation
T_i = sum of natural logtransformed data points for each wet air oxidation process.

(iv) - the sum of the squares within data sets (SSW) is computed:

$$SSW = \left[\sum_{i=1}^{k} \sum_{j=1}^{n_i} x_{i,j}^2 \right] - \sum_{i=1}^{k} \left[\frac{T_i^2}{n_1} \right]$$

where:

$x_{i,j}$ - the natural logtransformed observations (j) for wet air oxidation process (i).

(v) - the degrees of freedom corresponding to SSB and SSW are calculated. For SSB, the degree of freedom is given by k-1. For SSW, the degree of freedom is given by N-k.

(vi) - using the above parameters, the F value is calculated as follows:

$$F = \frac{MSB}{MSW}$$

where:

MSB = SSB/(k-1) and
MSW = SSW/(N-k).

A computational table summarizing the above steps is shown below.

Computational Table for the F Value

Source	Degrees of freedom	Sum of squares	Mean square	F
Between	K-1	SSB	MSB = SSB/k-1	MSB/MSW
Within	N-k	SSW	MSW = SSW/N-k	

Table C-2 presents the values used for the accuracy-corrected data to be used in the ANOVA calculation, and the F value results are presented in Table C-3. The comparisons of data indicate that process 3 achieves significantly better treatment than the other technologies.

Table C-1

F Distribution at the 95 Percent Confidence Level

$F_{0.95}$

Denominator degrees of freedom	Numerator degrees of freedom								
	1	2	3	4	5	6	7	8	9
1	161.4	199.5	215.7	224.6	230.2	234.0	236.8	238.9	240.5
2	18.51	19.00	19.16	19.25	19.30	19.33	19.35	19.37	19.38
3	10.13	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10
7	5.59	4.74	4.35	4.12	1.97	1.87	1.79	1.73	1.68
8	5.32	4.46	4.07	1.84	1.69	1.58	1.50	1.44	1.39
9	5.12	4.26	1.86	1.63	1.48	1.37	1.29	1.23	1.18
10	4.96	4.10	1.71	1.48	1.33	1.22	1.14	1.07	1.02
11	4.84	1.98	1.59	1.36	1.20	1.09	1.01	2.95	2.90
12	4.75	1.89	1.49	1.26	1.11	1.00	2.91	2.85	2.80
13	4.67	1.81	1.41	1.18	1.03	2.92	2.83	2.77	2.71
14	4.60	1.74	1.34	1.11	2.96	2.85	2.76	2.70	2.65
15	4.54	1.68	1.29	1.06	2.90	2.79	2.71	2.64	2.59
16	4.49	1.63	1.24	1.01	2.85	2.74	2.66	2.59	2.54
17	4.45	1.59	1.20	2.96	2.81	2.70	2.61	2.55	2.49
18	4.41	1.55	1.16	2.93	2.77	2.66	2.58	2.51	2.46
19	4.38	1.52	1.13	2.90	2.74	2.63	2.54	2.48	2.42
20	4.35	1.49	1.10	2.87	2.71	2.60	2.51	2.45	2.39
21	4.32	1.47	1.07	2.84	2.68	2.57	2.49	2.42	2.37
22	4.30	1.44	1.05	2.82	2.66	2.55	2.46	2.40	2.34
23	4.28	1.42	1.03	2.80	2.64	2.53	2.44	2.37	2.32
24	4.26	1.40	1.01	2.78	2.62	2.51	2.42	2.36	2.30
25	4.24	1.39	2.99	2.76	2.60	2.49	2.40	2.34	2.28
26	4.23	1.37	2.98	2.74	2.59	2.47	2.39	2.32	2.27
27	4.21	1.35	2.96	2.73	2.57	2.46	2.37	2.31	2.25
28	4.20	1.34	2.95	2.71	2.56	2.45	2.36	2.29	2.24
29	4.18	1.33	2.93	2.70	2.55	2.43	2.35	2.28	2.22
30	4.17	1.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21
40	4.08	1.23	2.84	2.61	2.45	2.34	2.25	2.18	2.12
60	4.00	1.15	2.76	2.53	2.37	2.25	2.17	2.10	2.04
120	1.92	1.07	2.68	2.45	2.29	2.17	2.09	2.02	1.96
∞	1.84	1.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88

Table C-2 Accuracy-Correct Data to Be Used in the ANOVA Calculation

Wet air oxidation process	Source	Acetonitrile		Acrylamide		Acrylonitrile		Total Cyanide		Benzene	
		Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
1	Tischler/Kocurek 1989	575	110	908	0	50	1	1,100	2.4	--	--
			254		(1,120)		0		2.2		--
			245		(1,205)		12		0.3		--
			270		107		(100)		5		--
			295		(1,007)		0		2.5		--
			0		200		20		0.6		--
			407		69		43		1.7		--
			215		(1,057)		8		0		--
2	Tischler/Kocurek 1989	178	(221)	520	(972)	12	11	1,100	0.6	--	--
3	BP Chemical 1989b	166	3.8	844	2.59	1,560	<0.02	1,244	3.9	0.17	0.013
		229	3.3	770	1.81	1,590	<0.02	1,300	4.0	0.18	0.013
		104	13.3	1,089	5.54	728	<0.02	1,460	0.7	0.07	0.011
		684	11.8	745	8.24	550	<0.02	1,899	4.6	0.42	0.011
4	Cyanamid 1989b	690	15.5	680	<1	420	0.65	90	0.7	<5	0.006
		720	11.4	690	<1	215	0.20	120	0.56	<5	0.01

( ) = Deleted in Section 5 because of poor operating conditions; therefore, the value is not incorporated into the ANOVA calculation.

Table C-3 F Value Determination for ANOVA Test

Constituent	Source	Degree of freedom	Sum of squares	Mean square	F	Critical value	Process (See Table C-2)	Conclusion
Acetonitrile	Between (B)	2	36.95	18.48	69.14	4.10	1,3,4	Nonhomogeneous
	Within (W)	10	2.672	0.2672				
	Between (B)	1	32.64	32.64	111.90	5.12	1,3	Nonhomogeneous
	Within (W)	9	2.625	0.2917				
	Between (B)	1	0.6198	0.6198	1.45	7.71	3,4	Homogeneous
	Within (W)	4	1.713	0.4282				
Acrylamide	Between (B)	2	31.90	15.95	47.61	5.14	1,3,4	Nonhomogeneous
	Within (W)	6	2.010	0.3350				
	Between (B)	1	19.74	19.74	49.11	6.61	1,3	Nonhomogeneous
	Within (W)	5	2.010	0.4020				
	Between (B)	1	2.399	2.399	6.67	7.71	3,4	Homogeneous
	Within (W)	4	1.438	0.3595				
Acrylonitrile	Between (B)	3	93.37	31.12	28.68	4.07	1,2,3,4	Nonhomogeneous
	Within (W)	8	8.68	1.085				
	Between (B)	1	84.77	84.77	74.31	5.59	1,3	Nonhomogeneous
	Within (WS)	7	7.986	1.141				
	Between (B)	1	11.15	11.15	64.21	7.21	3,4	Nonhomogeneous
	Within (W)	4	0.6946	0.1737				

Table C-3 (Continued)

Constituent	Source	Degree of freedom	Sum of squares	Mean square	F	Critical value	Process (See Table C-2)	Conclusion
Cyanide (total)	Between (B)	3	3,567	1.189	1.49	3.71	1,2,3,4	Homogeneous
	Within (W)	10	7.957	0.7957				
	Between (B)	1	0.7695	0.7695	0.87	5.12	1,3	Homogeneous
	Within (W)	9	7.915	0.8794				
	Between (B)	1	2.662	2.662	4.37	7.71	3,4	Homogeneous
	Within (W)	4	2.438	0.6094				
Benzene	Between (B)	1	0.2514	0.2514	6.35	7.71	3,4	Homogeneous
	Within (W)	4	0.1584	0.03959				